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(54) **Hair fixatives.**

(57) A hair treating method for imparting curl retention to hair in which at least one film forming ingredient is applied to the hair. The improvement utilizes as the film forming ingredient an organosilicon compound which is a pre-hydrolyzed organofunctional silane having silsesquioxane characteristic. Hair fixative compositions including the silane are also disclosed.

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This invention relates to new hair fixative compositions and to improved methods of providing curl retention to hair in which there is employed as the film forming ingredient certain pre-hydrolyzed organofunctional silanes.

Fixatives are designed to provide a temporary setting effect or curl to the hair and while the most common fixative is a hair spray which is designed to be applied to the hair after the hair has been blow dried, several specialty type fixatives can be applied either after the hair is towel dried or to dry hair, in order to provide more body and volume to the hair and to aid in styling, modeling and sculpting of the hair into unique new looks. This is followed by application of a hair spray in the form of an aerosol or pump spray to maintain the shape and style of the hair and provide gloss and sheen to the hair, in addition to a well groomed and natural appearance. Such specialty type fixatives are marketed under various names including styling gels, styling cremes, styling mousses, styling foams, styling sprays, styling spritz, styling mists, styling glazes, styling fixes; sculpting lotions, sculpting gels, sculpting glazes, sculpting sprays; glossing gels, glossing spritz; shaping gels; forming mousses; modeling spritz; finishing spritz; fixing gels; and setting lotions.

Whether the fixative is the more common hair spray or a specialty type fixative, it will typically include a film forming additive as the hair holding agent. The film forming additive should provide hair holding properties and curl retention, little flaking or powder on combing, rapid curing or drying on hair, nonstickiness and be easily removable by shampooing. Film forming additives are delivered by a solvent which is usually an alcohol such as ethanol or a mixture of an alcohol and water. In the case of aerosol formulations such as hairsprays and mousses, a propellant such as isobutane, butane, propane or dimethyl ether is an added part of the delivery system.

Examples of currently used film forming agents are shellac, polyvinylpyrrolidone-ethyl methacrylate-methacrylic acid terpolymer, vinyl acetate-crotonic acid copolymer, vinyl acetate-crotonic acid - vinyl neodeconate terpolymer, poly(vinylpyrrolidone-ethylmethacrylate methacrylic acid copolymer, vinyl methyl ether-maleic anhydride copolymer, octylacrylamide-acrylate-butylaminoethyl-methacrylate copolymer and poly(vinylpyrrolidone-dimethylaminoethylmethacrylate) copolymer and derivatives. These particular polymers are most suitable for alcohol based formulations such as hair sprays and pumps and are sometimes used in water-based hair fixative products.

Such resins contain carboxyl groups which must be neutralized to some degree to provide compatibility with water to facilitate removal by shampooing and to increase the flexibility of the film. However, the greater the extent of neutralization, the less resistant the film is to high humidity. Therefore, although these resins can be rendered water soluble by neutralization, water-based fixative systems are not practical because of poor hold.

Polyvinylpyrrolidone and certain quaternary ammonium compounds, most notably Polyquaternium-11 (an adopted name of the Cosmetic, Toiletry and Fragrance Association) are film forming additives used in completely water based fixative systems such as gels and mousses. However, these water soluble resins form films which are not resistant to high humidity. In fact, these polymers tend to be hygroscopic to the extent that exposure to high humidity actually softens and plasticizes the films through water absorption. Thus, a need exists for a fixative resin which is (i) completely water soluble without neutralization and provides high humidity resistance when applied from aqueous solutions, (ii) compatible with hydrocarbon propellants and (iii) can be used in all the possible solvent systems for this application.

In accordance with the present invention, a new hair fixative formulation is provided which includes an organosilicon film forming material. Specifically, the organosilicon film forming material is an organofunctional silane hydrolyzate. It is not new in the art to employ organosilicon compounds in hair fixative compositions. Nor is it new in the art to use silane type materials in hair fixatives. For example, organosilanes are disclosed in U.S. Patent No. 2,782,790, issued February 26, 1957; U.S. Patent No. 4,344,763, issued August 17, 1982; and in European Patent Application 85104416.4, published October 30, 1985, under Publication No. 0 159 628 A2. While these references disclose various hair treating, hair setting and hair waving methods which employ silanes, none of the prior art teaches the use of the particular pre-hydrolyzed organofunctional silane having silsesquioxane characteristic as disclosed herein.

In contrast to the organic film forming additives, the compositions of the present invention provide high humidity resistance from water, as well as ethanol-water solubility without neutralization. The polar functionality and the dispersability of the organosilicon materials permits the formation of solutions, emulsions, micro-emulsions or suspensions in water. The silane hydrolyzates can also be delivered as aerosol solvents or in volatile silicones, mineral oil or other non-volatile hydrocarbons. This range of solubility is made possible by the chain flexibility of the molecule and by incorporating varying levels of organofunctionality. Other advantages include nonirritability, excellent shampoo removability, good sheen, low buildup, lack of tackiness and reduced flaking.

This invention is directed to a hair treating method for imparting curl retention to hair in which at least one film forming ingredient is applied to the hair. The improvement utilizes as the film forming ingredient an organosilicon compound. The preferred organosilicon compound is a pre-hydrolyzed organofunctional silane having silsesquioxane characteristic.

This invention is also directed to a hair treating method for imparting curl retention to hair in which a film is formed on the hair and the film is an organosilicon compound which is a pre-hydrolyzed organofunctional silane having silsesquioxane characteristic.

The invention is further directed to hair fixative compositions for imparting curl retention to hair which include an organosilicon compound which is a pre-hydrolyzed organofunctional silane having silsesquioxane characteristic.

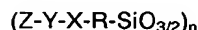
These and other features, objects and advantages, of the present invention will become more apparent when considered in light of the following detailed description thereof.

As noted above, the present invention relates to hair fixatives which utilize as the film forming ingredient a pre-hydrolyzed organofunctional silane having silsesquioxane characteristic. Such silanes have been found to exhibit improved curl retention in comparison to conventional organic systems and provide the advantages of ethanol solubility, water compatibility, nonirritability, excellent aesthetics on hair, good wet and dry combing, excellent shampoo removability, good sheen, improved hold, low buildup, nontacky and reduced flaking. The hydrolyzed silanes of the present invention also offer the added benefit that a plasticizer is not required, although plasticizers may be included in the fixative composition if desired.

Typical organic fixative systems include what are known in the trade as GANTREZ® resins which are polymers consisting of the partial ethyl ether of the polycarboxylic resin formed from vinyl methyl ester and maleic anhydride. One of the more popular GANTREZ® resins is GANTREZ® ES 225, a product of the GAF Corporation, Wayne New Jersey. GANTREZ® is also a trademark of the GAF Corporation. This resin has been the film forming ingredient in such products as WHITE RAIN® and FINAL NET®. Such resins are typically employed as an ethanol based pump spray.

Several commercial hair fixative formulations are water based and include deep conditioners, styling gels and mousses. While not primarily a hair fixative, the deep conditioners may contain a water soluble resin for imparting some degree of set retention. The most popular organic film forming ingredient in such water based organic systems is known in the trade as the GAFQUAT® resins. Such resins are also products of the GAF Corporation, Wayne, New Jersey, and GAFQUAT® is a trademark of that company. Exemplary of the commercial resins are GAFQUAT® 734 and GAFQUAT® 755, otherwise known under the designation Polyquaternium-11, an adopted name of the Cosmetic, Toiletry and Fragrance Association. While organosilicon compounds are not known to be water soluble, the hydrolyzed silanes of the present invention are soluble or compatible in water based systems and hence possess utility in such systems in place of the organic GAFQUAT® variety of resin currently employed in the art.

The pre-hydrolyzed organofunctional silanes of the present invention having silsesquioxane characteristic also have application in aqueous-alcohol based hair fixative systems. Aqueous ethanol, for example, is employed in some commercial spray-on pump and aerosol type products and mousses. The function of the alcohol in such systems is to promote faster drying of the formulation relative to the water based type system. In addition, the silanes of the present invention may be used in anhydrous alcohol systems whether the system is designed for aerosol delivery or delivery by means of a pump spray device. In the hair treating method in accordance with the present invention, the film forming ingredient is an organosilicon compound having in the molecule at least one moiety of the formula



wherein

X is a radical selected from the group consisting of amino, ammonium, quaternary amino, carbonyl, sulfonyl and amido or a sulfur or oxygen atom;

Y is an oxygen atom, a radical selected from the group consisting of alkylene, arylene, alkylarylene, alkyleneoxy, aryleneoxy, alkylaryleneoxy, carbonyl and phosphoryl or a covalent bond;

Z is hydrogen or a radical selected from the group consisting of alkyl, alkenyl, aryl, amino, amido, ammonium, hydroxy, carboxy, vinyl, vinylbenzene, epoxy, vinylbenzylamino, alkylacrylo, polyalkyleneoxy, metal hydroxyl, alkylcarbonyl, arylcarbonyl, morpholino and oxazolino;

R is a radical selected from the group consisting of alkylene, arylene, alkylarylene and alkenylene or an oxygenated, aminated, amidated or thiolated, substitution thereof; and

n is an integer from one to ten thousand.

These organosilicon compound are pre-hydrolyzed organofunctional silanes having silsesquioxane

characteristic and the organosilicon compound is applied to the hair as a mixture including a solvent. The organosilicon compound is present in the mixture at a level from about 0.1 to about fifty percent by weight based on the weight of the mixture. Preferably, the organosilicon compound is present in the mixture at a level from about three to about thirty percent by weight based on the weight of the mixture. The solvent may be water, a hydrocarbon, an alcohol or a blend of alcohol and water. Where the solvent is a hydrocarbon, it is preferred to employ materials such as dimethylether, liquefied petroleum gas, propane and isobutane. In the event the solvent is an alcohol, some appropriate materials are methanol, ethanol and isopropanol.

With regard to the compounds expressed in the above formula, the alkyl, alkenyl and alkylene radicals preferably contain from one to twenty carbon atoms. It should also be noted that where the composition bears a positive charge, the anion may be a weak acid carboxylate, sulfate, nitrate, benzoate, halide or other anion. Where the compound is aminofunctional, it may be protonated with a protonic acid, or neutralized without protonation with a Lewis acid. The compounds may be linear, cyclic or of ladder structure. Such compounds can also be dimerized, trimerized or partially dimerized or trimerized through the X, Y and Z groups. These compounds may be employed with fillers if desired. The organosilicon compounds in accordance with the present invention further may be soluble materials; micellar; capable of forming submicron aggregates such as vesicles or microemulsions; or liquid crystalline in structure depending on the solvent system employed. Such compounds may be homopolymers, copolymers, terpolymers or blends including other silicone or organic compositions.

One preferred compound in accordance with the present invention is a pre-hydrolyzed organofunctional silane having silsesquioxane characteristic and containing in the molecule at least one moiety of the formula



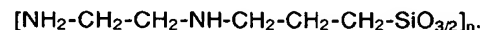
The interger n in the above formula can vary between one and about twenty. This pre-hydrolyzed silane can be applied to the hair as a mixture including a solvent and, in addition, if desired, at least one additional ingredient such as propellants, conditioners, surfactants, plasticizers, thickeners, preservatives and fragrances.

The silanes of the present invention were dissolved in ethanol and tested for curl retention. These formulations were compared to a commercial aerosol product containing about four to five percent by weight of the film forming resin ingredient RESYN® 28-2930 manufactured by National Starch and Chemical, Bridgewater, New Jersey. The hydrolyzed silanes of the present invention provided curl retentions beyond the curl retention obtained with the commercial product and at levels ranging from about one to five percent by weight of the silane. In experiments involving multiple hair tresses, the silanes of the present invention provided more consistent results than the corresponding commercial product. Similar results were achieved in tests comparing the hydrolyzed silane film formers of the present invention with another commercial product FINAL NET®. The results of these tests and their procedures are set forth below.

The following examples are set forth in order to illustrate in more detail the concepts embodied by the present invention.

Example I

Into a three necked round bottom flask equipped with a stirrer and thermometer was placed 66.2 grams of ethylenediamino-propyltrimethoxy silane of the formula $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$. To the flask was added thirty grams of a fifty-fifty blend of n-octanol and n-decanol. The silane and the alcohol blend was mixed thoroughly. To the mixture was slowly added 3.8 grams of deionized water and the contents of the flask was allowed to mix for about one hour. The flask was heated to 160° C. while stripping methanol. After the flask was cooled, the product was recovered and identified to be a pre-hydrolyzed organofunctional silane having silsesquioxane characteristic and having in the molecule at least one moiety of the formula



Example II

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The hydrolyzed silane of Example I was formulated into a hair fixative composition by mixing the hydrolyzed silane with ethanol in order to provide various fixative formulations containing one, two, three and five percent by weight of the silane. These silane hair fixative formulations were evaluated for curl retention and compared to commercial hair fixative products in accordance with the procedures set forth below. The results of such evaluations and comparisons are provided in the accompanying Tables.

Example III

Hair fixative formulations were evaluated by employing six inch hair tresses of approximately two grams of untreated human hair. Each tress was made by gluing the top part of the hair to a 2" x 2" plastic tab. After drying on the tab, the hair was trimmed to six inches. Each tress was then cleaned with an anionic/amphoteric shampoo of the following formulation:

Distilled Water	61.45%
Methylchlorisothiazolinone and methylisothiazolinone	0.05%
Ammonium Lauryl Sulfate	35.00%
Lauramide DEA	3.00%
Sulfuric Acid	q.s.
Ammonium Chloride	0.50%

The tress was first rinsed for 15 minutes under 40° C. tap water and 0.5 cc of the above shampoo was applied. Shampooing for 30 seconds was followed by a 30 second rinse. The tresses were then set on plastic rollers approximately 1/2 in. in diameter and allowed to dry overnight. Hair fixative formulations were applied to the hair either by dripping on 0.5 g or by spraying on 0.3 g. If the drip application was used, the hair was combed three times and reset on a roller. If the resin solution was delivered from a pump, the hair was not reset. The solution was allowed to cure on the hair for a period of one to two hours for ethanol-based and overnight for water-based formulations. The dried tresses were hung in a constant humidity chamber at 90 percent relative humidity and initial readings were taken as well as additional readings at predetermined intervals. If the tress was reset, the roller was removed prior to exposure.

Curl retention was calculated as the extended length minus the length at the end of the predetermined interval divided by the extended length minus the initial length. Tables I and II represent curl retention after 24 hours of exposure and evidence excellent performance of the silane hydrolyzate at low add-on levels in comparison to the organic control.

TABLE I

Percent Silane in Ethanol	Curl Retention (Percent)
1.0	96
2.0	96
3.0	96
5.0	94

TABLE II

Percent GANTREZ in Ethanol	
1.0	0
2.0	0
3.0	73

Example IV

Into a three neck round bottom flask equipped with a stirrer, thermometer and nitrogen inlet was placed 60 grams of ethylenediaminopropyltrimethoxy silane. To the flask was added 425 grams of 200 proof ethanol and 15 grams de-ionized water while stirring. The mixture was refluxed under nitrogen for more than one hour. After cooling, the solution was poured out into evaporating equipment and the solvent was evaporated off at room temperature. The solid was then redissolved in 150 grams 200 proof ethanol in a flask under nitrogen while heating.

Example V

The hydrolyzed silane of Example IV was formulated into a hair fixative composition by mixing the hydrolyzed silane with ethanol in order to provide various fixative formulations containing three, five and ten percent by weight of the silane.

EXAMPLE VI

The hair fixative formulations of Example V were evaluated according to the procedure described in Example III. The organic resin GANTREZ ES225 was used as the control comparison. The results of these evaluations are given below.

TABLE III

<u>Percent Silane in Ethanol</u>	<u>Curl Retention (Percent)</u>
3.0	86
5.0	98
10.0	98
<u>Percent Gantrez in Ethanol</u>	
3.0	73
5.0	93
10.0	98

Example VII

Part A: Into a 4 oz. bottle was added 40 grams 200 proof ethanol and 4 grams methyltrimethoxysilane of the formula $\text{CH}_3\text{Si}(\text{OCH}_3)_3$. Part B: Into another 4 oz. bottle was added 1.5 grams de-ionized water and 0.6 grams ethylenediaminopropyltrimethoxysilane. After mixing both parts, Part A was added to Part B.

Example VIII

Part A: Into a 4 oz. bottle was added 40 grams 200 proof ethanol and 4 grams propyltrimethoxysilane of the formula $\text{CH}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$. Part B: Into another 4 oz. bottle was added 1.5 grams de-ionized water and 0.6 grams ethylenediaminopropyltrimethoxysilane. After mixing, Part A was added to Part B.

Example IX

The materials made in Examples VII and VIII were evaluated as hair fixatives without further dilution or modification. The procedures used were those in Example III and results are given below.

TABLE IV

Solution	Percent Silane in Ethanol	Curl Retention (Percent)
Example VII	8.7	98
Example VIII	8.7	99

Example X

Into a 4 oz. glass bottle was added 36 grams of deionized water. While stirring, 4.0 grams of ethylenediaminopropyltrimethoxysilane was slowly added. Stirring was continued to insure complete mixing. At least 16 hours was allowed to elapse prior to evaluation to ensure complete hydrolysis.

Example XI

Example X was repeated using the silane 3-(trimethoxysilyl)propyldimethyloctadecyl ammonium chloride of the formula $\text{Cl}(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)_2\text{N}^+\text{C}_{18}\text{H}_{37}$.

Example XII

Example X was repeated using sodium-3-trihydroxysilylpropylmethyl phosphonate of the formula $(\text{HO}^-)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OP}=\text{O}(\text{CH}_3)\text{O}^-\text{Na}^+$.

Example XIII

The materials made in Examples X, XI and XII, were evaluated as hair fixatives without further dilution or modification. The procedures used were those in Example III and results are given in Table V including comparisons to PVP K-30 (polyvinylpyrrolidone) and GAFQUAT® 755N.

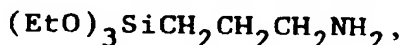
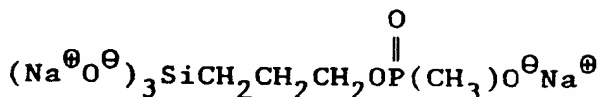
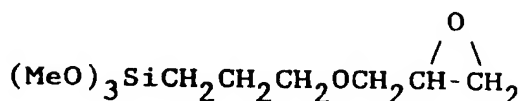
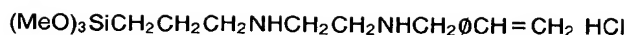
TABLE V

<u>Solution</u>	<u>Percent Silane in Water</u>	<u>Curl Retention (Percent)</u>
Example XII	10	93
Example XIII	10	94
Example XIV	10	94
<u>Solution</u>	<u>Percent Resin in Water</u>	
PVP K-30	10	0
GAFQUAT® 755N	10	0

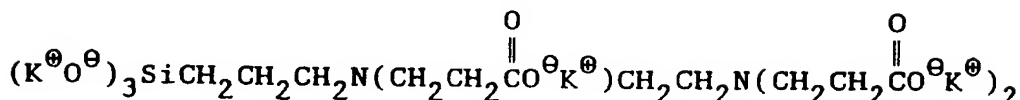
PVP K-30 is a polyvinylpyrrolidone polymer with an average molecular weight of 40,000. GARQUAT® 755N is a quaternized copolymer of vinylpyrrolidone and dimethylaminoethyl methacrylate with an average molecular weight of 1,000,000 and the CTFA designation of Polyquaternium-23.

Compounds preferred in accordance with the present invention are those compounds which are produced from the following silanes as starting materials:

$(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
 $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
 $\text{Cl}^-(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2(\text{Me})_2\text{N}^+\text{C}_{18}\text{H}_{37}$
 $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$



and



The compositions of this invention may contain an emulsifying agent selected from the group consisting of anionic, amphoteric, nonionic, cationic and zwitterionic surfactants. Suitable anionic detergents include sulfonated and sulfated alkyl, aralkyl and alkaryl anionic detergents; alkyl succinates; alkyl sulfosuccinates and N-alkyl sarcosinates.

Surfactants generally classified as amphoteric or ampholytic detergents include, among others, cocoamphocarboxyglycinate, cocoamphocarboxypropionate, cocobetaine, N-cocamidopropyltrimethylglycine and N-lauryl-N-carboxymethyl-N-(2-hydroxyethyl)ethylenediamine. Other suitable amphoteric detergents include the quaternary cycloimidates, betaines and sultaines disclosed in U.S. Patent No. 3,964,500.

The compositions of this invention may contain a nonionic surfactant. The nonionic surfactants of the present invention are selected from the group consisting of fatty acid alkanolamide and amine oxide surfactants.

Appropriate cationic surfactants in accordance with the present invention include quaternary ammonium salts of primary, secondary and tertiary fatty amines. Zwitterionic surfactants which may be employed are quaternary ammonium, phosphonium and sulfonium compounds containing aliphatic substituents one of which is carboxy, phosphate, phosphonate, sulfate or sulfonate functional.

Other adjuvants may be added to the compositions of this invention such as plasticizers, thickeners, perfumes, colorants, electrolytes, pH control ingredients, anti-microbials, antioxidants, ultraviolet light absorbers and medicaments. When the fixative is in the form of a gel or lotion, it is sometimes preferred to employ a thickener in the compositions to facilitate the hand application of the composition to the hair. Thickeners are preferably used in sufficient quantities to provide a convenient viscosity. For example, viscosities within the range of 400 to 6000 cps are preferred for lotions. Higher viscosities are preferred for gels whereas lower viscosities are preferred for sprays.

Suitable thickeners, include, among others, sodium alginate, gum arabic, polyoxyethylene, guar gum, hydroxypropyl guar gum, cellulose derivatives such as methyl-cellulose, methylhydroxypropylcellulose, hydroxypropylcellulose, polypropylhydroxyethylcellulose, starch and starch derivatives such as hydroxyethylamylose and starch amylose, locust bean gum, electrolytes such as NaCl, saccharides such as fructose and glucose and derivatives of saccharides such as PEG-120 methyl glucose dioleate. Preferred thickeners include the cellulose derivatives and saccharide derivatives. The glucose derivative, PEG-120 methyl glucose dioleate, is especially preferred in the present invention. Electrolytes including sodium chloride and ammonium chloride provide thickening particularly in aqueous systems and may also be employed in accordance with the present invention.

Representative plasticizers that may be employed include polypropylene glycol, glycerine and polysiloxanes. Siloxane polymers such as polydimethylsiloxane, cyclic polydimethylsiloxane, phenylpolydimethylsiloxane and polydimethylsiloxane with methylene and or propylene oxide side chains, are particularly preferred in accordance with the present invention.

The perfumes which can be used in the compositions are the cosmetically acceptable perfumes. Colorants are used to confer a color to the composition and may generally be used. Although not required, it is preferred to employ an acid or base to adjust the pH within the range of 5 to 9 or more preferably within the range of 6 to 8 in the compositions of this invention. Any water soluble acid such as a carboxylic acid or a mineral acid is suitable. For example, suitable acids include mineral acids such as hydrochloric,

sulfuric and phosphoric, monocarboxylic acids such as acetic acid, lactic acid or propionic acid; and polycarboxylic acids such as succinic acid, adipic acid and citric acid. Where a base is required, organic amines such as 2-amino-2-methyl-1-propanol are appropriate.

If for special purposes conditioners are desired, they may be added. For example, any of the well-known organic cationic hair conditioning components may be added. Some cationic conditioning components that may be used in the present invention to provide hair grooming include quaternary nitrogen derivatives of cellulose ethers, homopolymers of dimethyldiallyl-ammonium chloride, copolymers of acrylamide and dimethyldiallylammonium chloride, homopolymers or copolymers derived from acrylic acid or methacrylic acid containing cationic nitrogen functional groups attached to the polymer via ester or amide linkages, polycondensation products of N,N'-bis-(2,3-epoxypropyl)piperazine or of piperazine-bis-acrylamide and piperazine, poly(dimethylbutenylammonium chloride)- α,ω -bis-(triethanol-ammonium) chloride and copolymers of vinylpyrrolidone and acrylic acid esters with quaternary nitrogen functionality. The above cationic organic polymers and others are described in more detail in U.S. Patent No. 4,240,450. Other categories of organic conditioners may also be employed such as proteins, monomeric organic quaternaries and betaines. Silicone conditioning agents may also be employed such as cyclomethicone, dimethicone, phenyldimethicone, dimethicone copolyol, amodimethicone and trimethylsilylamodimethicone.

A preservative may be required and representative preservatives which may be employed include about 0.1-0.2 weight percent of compounds such as formaldehyde, dimethyloldimethylhydantoin, 5-bromo-5-nitro-1,3-dioxane, methyl and propyl para-hydroxybenzoates and mixtures of such benzoates with sodium dehydroacetate, sorbic acid and imidazolidinyl urea.

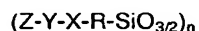
The compositions of the present invention may also be formulated to include dyes, colorants, reducing agents, neutralizing agents and preservatives, necessary for their application as permanent wave systems or hair dyes, for example. The active formulation can be applied in several different forms including lotions, gels, mousses, aerosols and pump sprays, for example, and as conditioners and shampoos. The active ingredient includes a carrier and suitable carrier fluids for hair care formulations are water as well as, for example, such fluids as alcohols namely ethanol or isopropanol, hydrocarbons and halogenated hydrocarbons such as mineral spirits and trichloroethane, supercritical fluids such as supercritical carbon dioxide and nitrogen, cyclic siloxanes and aerosol propellants. In those instances where it is desired to incorporate the active in the form of either an emulsion or microemulsion, such emulsions may be prepared in accordance with either U.S. Patent No. 4,501,619, issued February 26, 1985, which is directed to emulsions or U.S. Patent No. 4,620,878, issued November 4, 1986, relating to microemulsions.

When the composition is intended for aerosol application, propellant gases can be included such as carbon dioxide, nitrogen, nitrous oxide, volatile hydrocarbons such as butane, isobutane or propane and chlorinated or fluorinated hydrocarbons such as dichlorodifluoromethane and dichlorotetrafluoroethane or dimethylether. Where the solvent system is alcohol free, mechanical and chemical drying agents may also be employed in spray and aerosol formulations.

It will be apparent from the foregoing that many other variations and modifications may be made in the compounds, compositions and methods, described herein, without departing substantially from the essential features and concepts of the present invention. Accordingly, it should be clearly understood that the forms of the invention described herein are exemplary only and are not intended as limitations on the scope of the present invention as defined in the appended claims.

Claims

1. In a hair treating method for imparting curl retention to hair in which at least one film forming ingredient is applied to the hair, the improvement comprising utilizing as the film forming ingredient an organosilicon compound having in the molecule at least one moiety of the formula



wherein

X is a radical selected from the group consisting of amino, ammonium, quaternary amino, carbonyl, sulfonyl and amido or a sulfur or oxygen atom;

Y is an oxygen atom, a radical selected from the group consisting of alkylene, arylene, alkylarylene, alkyleneoxy, aryleneoxy, alkylaryleneoxy, carbonyl and phosphoryl or a covalent bond;

Z is hydrogen or a radical selected from the group consisting of alkyl, alkenyl, aryl, amino, amido, ammonium, hydroxy, carboxy, vinyl, vinylbenzene, epoxy, vinylbenzylamino, alkylacrylo, polyalkyleneoxy, metal hydroxyl, alkylcarbonyl, arylcarbonyl, morpholino and oxazolino;

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R is a radical selected from the group consisting of alkylene, arylene, alkylarylene and alkenylene or an oxygenated, aminated, amidated or thiolated, substitution thereof; and
n is an integer from one to ten thousand.

- 5 2. The method of claim 1 in which the organosilicon compound is applied to the hair as a mixture including a solvent and in which the organosilicon compound is present in the mixture at a level from about 0.1 to about fifty percent by weight based on the weight of the mixture.
- 10 3. The method of claim 2 in which the pre-hydrolyzed organofunctional silane having silsesquioxane characteristic has in the molecule at least one moiety of the formula $[\text{NH}_2\text{-CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{SiO}_{3/2}]_n$.

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(54) **Hair fixatives.**

(57) A hair treating method for imparting curl retention to hair in which at least one film forming ingredient is applied to the hair. The improvement utilizes as the film forming ingredient an organosilicon compound which is a pre-hydrolyzed organofunctional silane having silsesquioxane characteristic. Hair fixative compositions including the silane are also disclosed.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 179 347 (REVLON INC) * page 7, line 8 - line 27; claims 1-14 * ----	1-3	A61K7/11 A61K7/06
A,D	US-A-4 344 763 (E. TOLGYESI ET AL.) * column 2, line 60 - column 3, line 6; claims 1-10 * ----	1-3	
A,D	EP-A-0 159 628 (REVLON INC.) * page 5, line 1 - line 28; claims 1-14 * ----	1-3	
A	EP-A-0 174 097 (DOW CORNING CORPORATION) * claims 1-10 * -----	1-3	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A61K
Place of search BERLIN		Date of completion of the search 21 DECEMBER 1992	Examiner SIATOU E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

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